Investigations on Sorption, Diffusion and Permeation of Chloroalkanes and Chloroalkenes through Fluoroelastomeric Membrane

VII.1 ABSTRACT: Sorption, diffusion and permeation of halogenated liquids such as chloroform, dichloromethane, carbontetrachloride, 1,2-dichloroethane, 1,1,2,2-tetrachloroethane, trichloroethylene and tetrachloroethylene into commercial fluoroelastomer (FC-2177 D) have been studied at 30, 40 and 50°C using sorption gravimetric method. The concentration-independent diffusion coefficients were calculated using Fick’s equation from the initial linear portion of the sorption curves. The liquid concentration profiles have also been computed using analytical solution of Fick’s equation with the appropriate initial and boundary conditions and these were presented as a function of penetration depths of molecular migration and time of immersion. These results have been discussed in terms of the molecular size of the liquid penetrants and temperature. The transport phenomenon was found to follow the anomalous behaviour. From a temperature dependence of diffusion and permeation coefficients, the Arrhenius activation parameters have been estimated. The activation energies for diffusion and permeation do not exhibit any systematic dependence on the size of the penetrating molecules, but these are influenced by the nature of the liquids. None of the liquids showed any degradative effects on the membrane.

Results of this Chapter are communicated to J Appl Polym Sci

Chapter VII
VII.2 INTRODUCTION

The diffusion of small molecules through polymer membranes is an important phenomenon in many areas of science and engineering [1,2]. For example, the diffusivity in polymer films and membranes is important in connection with the use of polymers as barrier coatings in packaging applications [3], and for separation science applications [1,4]. The diffusion of organic molecules in polymers has implications even further afield with such small molecules playing important roles in polymer industries as plasticizers, fillers and biocides, etc. Further, organic solvents are also used to remove small organic impurities of oligomers from poly(ethyleneterphthalate) (PET) films for use as high specification substrates [5]. Therefore, an understanding of the dimensional stability and integrity of the polymeric materials in the presence of such liquids are very important as far as their wide variety of applications are concerned [6].

Synthetic polymer membranes with tailored morphology, good physical/mechanical properties with a fair degree of dimensional and chemical stability, have been widely used in commercial applications. In all these applications, the molecular transport of organic liquids into polymeric membranes is known to occur under the influence of chemical potential gradient. However, suitability of a particular polymeric material for a specified application is determined by its sorption characteristics as well as diffusion anomalies.

The polymer-solvent interaction has been extensively studied and reviewed by many researchers [7-12]. Molecular transport of organic penetrants through
polymeric materials is controlled by two mechanisms: chemical potential gradient driven diffusion associated with a companion stress evaluation. The relative magnitude of these two processes will decide which mechanism is predominant. When membrane swelling is not observed, the transport mechanism is mainly due to molecular diffusion and the advance of the penetrant front is proportional to $t^n$ with $n \approx \frac{1}{2}$. This situation is referred to as Case I mechanism (Fickian diffusion). When membrane swelling is observed, the stress in the viscoelastic membrane is altered significantly and $n \approx 1$. This situation is referred to as Case II mechanism (non-Fickian diffusion). However, deviations from the Fickian behaviour are also reported [13-15]. Rate of diffusion through a polymer membrane depends on the polymer structure, type of crosslinking, crosslinking density, size of the penetrants, temperature, etc. Unnikrishnan and Thomas [16], and Mathew et al. [17] investigated the role of the nature of crosslinks, fillers, etc. on the sorption and diffusion of aromatic hydrocarbons and styrene monomer through crosslinked natural rubber. Recently in our laboratory, we have studied [13,14] the sorption and diffusion behaviour of organic liquids through tetrafluoroethylene/propylene copolymers and found that the mechanism of diffusion follows anomalous Fickian trend. Chiang and Setton [18] used the solvent sorption methods to investigate the morphology of a styrene-butadiene-styrene-block copolymer. Importance of diffusion and permeation studies persists because a detailed experimental analysis is needed for designing economically viable barrier materials and membranes.
Many instances of ground water contaminations by organic liquids have been reported [19-21]. Of the identified organic contaminants in subsurface drinking water supplies, halogenated organics have been detected at the highest concentration levels and with the greatest frequency [22]. The transport, distribution and fate of such chemicals in both ground water and surface water are dependent on their sorptive interactions with soils, sediments and aquifer solids. When polymers are used as liners in hazardous waste pond applications or even as a container to transport hazardous/aggressive chemicals, solvent interaction with the barrier materials should be evaluated before field applications. Therefore, the present work aims to study the diffusion anomalies of halogenated liquids through Fluorel copolymer membrane (FC-2177D). The sorption data were used to study the transport mechanism and to calculate diffusion and permeation coefficients. In addition, analytical solution of Fick's equation has been used to calculate the liquid concentration profiles at different times and depths of liquids inside the membrane material. The temperature dependent transport coefficients have been used to estimate the Arrhenius activation parameters.

**VII.3 EXPERIMENTAL**

**VII.3.1 Reagents/chemicals**

The organic penetrants, such as chloroform, carbontetrachloride and 1,2-dichloroethane were obtained from Sisco Chem. Industries, Mumbai, India. Dichloromethane, 1,1,2,2-tetrachloroethane, trichloroethylene and trichloroethylene were procured from s. d. fine Chemicals Ltd., Mumbai, India.
All the chemicals are of analytical grade and were used without further purification. Other physical properties of these liquids are presented in Chapter II (Table II.2).

**VII.3.2 Materials**

Fluorel FC-2177D is a medium viscosity-grade copolymer designed for injection molding and sealing components that meet the major fluoroelastomer O-ring specifications. The typical properties of the fluoroelastomer are: specific gravity, 1.80; color, opaque off-white; solubility, in ketones and esters; mooney viscosity, approximately 34 ML 1 + 10 at 121°C. The sample press-cured for 7 min at 177°C possesses the following mechanical properties: tensile strength, 1865 psi; elongation at break, 240 %; hardness (shore A), 75. The sample was compounded with standard fillers and ingredients utilized in typical fluoroelastomer formulations.

**VII.3.3 Sorption Experiments**

The circularly cut disc-shaped membrane samples of ~ 2 cm in diameter were dried in a vacuum desiccator for 45 h over anhydrous CaCl₂ before performing the sorption experiments. These samples were then immersed in about 15 – 20 mL of liquids taken in airtight bottles and were maintained at 30, 40 and 50°C in an electronically controlled oven within an accuracy of ± 0.5°C. These samples were then immediately weighed on a top loading digital Mettler balance with an accuracy of ± 0.01 mg. The rest of the procedure was followed as per the detailed procedure given in Chapter II.5.
VII.4 RESULTS AND DISCUSSION

VII.4.1 Sorption Kinetics

The sorption coefficients data of all the liquids with fluoroelastomeric membranes measured at 30, 40 and 50° C are calculated using the Eq. II.3 and these are presented in Table VII.1, while the mol % sorption plots are displayed in Figs. VII.1-VII.3, respectively, for 30, 40 and 50° C.

Table VII.1 Physical Properties and Sorption Coefficients of Chloroalkanes and Chloroalkenes through Fluoroelastomeric Membrane.

<table>
<thead>
<tr>
<th>Liquids</th>
<th>Molar volume (cm^3/mol)</th>
<th>Sorption coefficients (S) (mol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30°C</td>
<td>40°C</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>64.5</td>
<td>0.0103</td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>79.4</td>
<td>0.1210</td>
</tr>
<tr>
<td>Chloroform</td>
<td>80.7</td>
<td>0.1070</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>90.0</td>
<td>0.0477</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>97.1</td>
<td>0.0076</td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>102.7</td>
<td>0.0046</td>
</tr>
<tr>
<td>1,1,2,2-Tetrachloroethane</td>
<td>105.8</td>
<td>0.0074</td>
</tr>
</tbody>
</table>

It is observed that the shapes of the curves, the equilibrium uptake value and time to attain the equilibrium sorption are dependent upon the size of the liquid molecules. For instance, dichloromethane with lower molar volume (64.5 cm^3/mol) takes shorter time to attain equilibrium saturation when compared to all
other chloroalkanes as shown in Figure VII.1. However, while comparing the uptake values of dichloromethane and 1,2-dichloroethane at 30°C, it is observed that the equilibrium sorption for dichloromethane is lower than that of 1,2-dichloroethane, although its molar volume is lower than that of 1,2-dichloroethane.

![Figure VII.1](image)

**Fig. VII.1** Plots of $M_t/M_\infty$ versus square root of time for fluoroelastomer 30°C with (■) dichloromethane, (▲) 1,2-dichloroethane, (●) chloroform, (◇) trichloroethylene, (□) carbontetrachloride, (△) 1,1,2,2-tetrachloroethane and (○) tetrachloroethylene.
Fig.VII.2 Plots of $M_t/M_\infty$ versus square root of time for fluoroelastomer at 40°C with
(▲) 1,2-dichloroethane, (●) chloroform, (◇) trichloroethylene, (□) carbontetrachloride,
(Δ) 1,1,2,2-tetrachloroethane and (○) tetrachloroethylene.

Fig.VII.3 Plots of $M_t/M_\infty$ versus square root of time for fluoroelastomer at 50°C with (▲)
1,2-dichloroethane, (●) chloroform, (◇) trichloroethylene, (□) carbontetrachloride, (Δ)
1,1,2,2-tetrachloroethane and (○) tetrachloroethylene.
In addition, the equilibrium sorption is decreased after reaching a maximum. Such decrease in sorption may be either interpreted as (i) solvent loss due to desorption/evaporation, or (ii) mass loss due to membrane leaching effects. But in the present case, the former appears to be more likely because of the low boiling temperature of dichloromethane and hence, the sorption data was not able to obtain for dichloromethane at higher temperatures, i.e., at 40 and 50°C. Of all the chloroalkanes studied, 1,2-dichloroethane exhibits the highest sorption at all the temperatures followed by chloroform, carbontetrachloride and 1,1,2,2-tetrachloroethane, which have higher molar volumes of 80.7, 97.1 and 105.8 cm³/mol, respectively. Further, the sorption values have a systematic trend with the size of the penetrants and in accordance, the sorption coefficients decrease with increasing the size of the liquid molecules. On the other hand, between the chloroalkenes, trichloroethylene exhibits higher sorption curves than that of tetrachloroethylene. This is also strictly in accordance with the size of the liquid penetrants.

In all the cases, the sorption curves increased with increasing temperature, i.e., sorption generally increases with increasing temperature. This is because of the creation of extra free-volume within the polymer matrix due to increased segmental motion of the polymer chains at higher temperature.

**VII.4.2 Diffusion and Permeation Coefficients**

The results of diffusion coefficients are calculated using the Eq. III.5, presented in Table VII.2. It is observed that the diffusion coefficients decreased from
dichloromethane to 1,1,2,2-tetrachloroethane as the size of the migrating liquids increased at all temperatures, suggesting the dependence of $D$ on the molecular size of penetrant. However, chloroform, trichloroethylene and carbontetrachloride show significantly higher $D$ values than those of dichloromethane and 1,2-dichloroethane. It indicates that the $D$ values of these liquids are neither dependent on the size of liquid penetrants nor on the dipole moment of liquids. Similar observations were noticed by Aminabhavi et al. [23] in case of Santoprene membrane (polymeric blend of ethylene-propylene random copolymer and isotactic polypropylene). This clearly signifies that transport phenomenon not only depends on the size of the migrating liquids, but also on the specific nature of liquids and the molecular interactions between the liquid penetrant and the membrane. The $D$ values calculated at 30°C vary according to the sequence: 1,1,2,2-tetrachloroethane $<\ tetrachloroethylene <\ 1,2$-dichloroethane $<\$ carbontetrachloride $<\$ dichloromethane $<\$ chloroform $<\$ trichloroethylene.

Permeability coefficients ($P$), calculated from the kinetic gravimetric sorption experiments using the Eq. III.6 are also included in Table VII.2. It is also observed that permeability results follow the same pattern as those of diffusion coefficients in the investigated temperature range.
Table VII.2 Diffusion ($D$) and Permeation ($P$) Coefficients of Chloroalkanes and Chloroalkenes at Different Temperatures through Fluoroelastomeric Membrane.

<table>
<thead>
<tr>
<th>Liquids</th>
<th>Dipole moment ($\mu$)</th>
<th>$D \times 10^8$ (cm$^2$/s)</th>
<th>$P \times 10^8$ (cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>30°C</td>
<td>40°C</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>1.14</td>
<td>2.85</td>
<td>–</td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>1.83</td>
<td>2.15</td>
<td>3.65</td>
</tr>
<tr>
<td>Chloroform</td>
<td>1.15</td>
<td>5.75</td>
<td>7.82</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>0.80</td>
<td>5.92</td>
<td>6.72</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>0.00</td>
<td>2.62</td>
<td>3.15</td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>0.00</td>
<td>1.52</td>
<td>3.41</td>
</tr>
<tr>
<td>1,1,2,2-Tetrachloroethane</td>
<td>1.71</td>
<td>0.52</td>
<td>0.86</td>
</tr>
</tbody>
</table>

VII.4.3 Concentration Profiles

The concentration profiles have been calculated from Eq. III.7 with the procedures suggested earlier [24, 25-28]. These profiles have been calculated at different membrane thickness (i.e., penetration depths of the liquids) and at different time intervals during sorption experiments. Some representative graphs at different temperatures are presented in Figs. VII.4-VII.7 for 1,2-dichloroethane, 1,1,2,2-tetrachloroethane, trichloroethylene and tetrachloroethylene, respectively. It is observed that the different liquids show different depths of penetration.
ingression), and this depends on the time needed to attain equilibrium sorption as well as the temperature. Noticeable effects of the temperature on the shapes of the concentration profiles are prevalent in all the cases. For instance, at 50°C, because of the higher diffusivity of the liquids, the concentration profiles also exhibit higher values than those at 30 and 40°C. In addition, concentration profiles of the liquids vary with their diffusivity values.

Fig. VII.4(A) Concentration profiles calculated from Eq. III.7 for 1,2-dichloroethane through fluorocelastomer membrane at (A) 30°C, for (o) 25, (Δ) 50, (□) 100, (◊) 120, (•) 200, (▲) 300 and (■) 500 min.
Figs. VII.4(B & C) Concentration profiles calculated from Eq. III.7 for 1,2-dichloroethane through fluoroelastomer membrane at (B) and (C) 50°C. Symbols are the same as in Fig. VII.4(A).
Figs. VII.5(A & B) Concentration profiles calculated from Eq. III.7 for 1,1,2,2-tetrachloroethane through fluoroelastomer membrane at (A) 30 and (B) 40°C. Symbols are the same as in Fig. VII.4(A).
Fig. VII.5(C) Concentration profiles calculated from Eq. III.7 for 1,1,2,2-tetrachloroethane through fluoroelastomer membrane at (C) 50°C. Symbols are the same as in Fig. VII.4(A).

Fig. VII.6(A) Concentration profiles calculated from Eq. III.7 for trichloroethylene through fluoroelastomer membrane at (A) 30°C. Symbols are the same as in Fig. VII.4(A).
Figs. VII.6(B & C) Concentration profiles calculated from Eq. III.7 for trichloroethylene through fluoroelastomer membrane at (B) 40 and (C) 50°C. Symbols are the same as in Fig. VII.4(A).
Figs.VII.7(A & B) Concentration profiles calculated from Eq. III.7 for tetrachloroethylene through fluoroelastomer membrane at (A) 30 and (B) 40°C. Symbols are the same as in Fig.VII.4(A).
Fig. VII.7(C) Concentration profiles calculated from Eq. III.7 for tetrachloroethylene through fluoroelastomer membrane at (C) 50°C. Symbols are the same as in Fig. VII.4(A).

The diffusion coefficients of 1,2-dichloroethane is higher than that of 1,1,2,2-tetrachloroethane and hence, its concentration profiles are higher at all temperatures (see Figs. VII.4 and VII.5). Similarly, in case of trichloroethylene, diffusivity is quite high as compared to tetrachloroethylene and so are its concentration profile values quite higher than that of tetrachloroethylene as seen from the Figs. VII.6 and VII.7, respectively. Therefore, the profiles vary according to the diffusion values of the liquids. The similar trend is also observed for other liquids, but these plots are not displayed to reduce the number of plots.
**VII.4.4 Transport Mechanism**

In order to investigate the nature of the transport processes, we have fitted the mol% sorption data before the completion of 55% equilibrium to an empirical equation III.8. The parameters $n$ and $K$ have been estimated by the method of least squares at the 95% confidence limit. These data are presented in Table VII.3. Even though the values of $n$ are indicative of the nature of diffusive transport, but in these systems we have not been able to make any distinctive correlation between the values of $n$ and the nature of the sorption curves. In all the cases, the values of $n$ range between 0.50 and 0.59, signifying slight deviations from the Fickian diffusion and following anomalous transport behaviour, as is normally the case for elastomers [25-28]. Further, these results do not show any systematic variation with the temperature. However, the magnitude of $K$ implies that the nature of the polymer-liquid interaction varies according to the nature of the liquids. In all the cases, $K$ increases with increasing temperature. This further suggests that the diffusion of chloroalkanes and chloroalkenes into the polymer is an activated process and at higher temperatures the liquid molecules have higher thermal energies.
Table VII.3 Estimated Parameters of \( n \) and \( K \) for Chloroalkanes and Chloroalkenes Calculated from Eq. III.8 at Different Temperatures for Fluoroelastomeric Membrane.

<table>
<thead>
<tr>
<th>Liquids</th>
<th>( n )</th>
<th>( K )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30°C</td>
<td>40°C</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>0.50</td>
<td>-</td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>0.52</td>
<td>0.53</td>
</tr>
<tr>
<td>Chloroform</td>
<td>0.51</td>
<td>0.57</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>0.55</td>
<td>0.53</td>
</tr>
<tr>
<td>Carbontetrachloride</td>
<td>0.50</td>
<td>0.55</td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>0.53</td>
<td>0.57</td>
</tr>
<tr>
<td>1,1,2,2-Tetrachloroethane</td>
<td>0.54</td>
<td>0.52</td>
</tr>
</tbody>
</table>

VII. 4.5 Activation Parameters

Both diffusion and permeation are found to be greatly affected by temperature. As expected, these parameters showed an increase with rise in temperature. This is attributed to increased segmental motion of the polymer chains, creating the additional free volume for greater solvent transport. This effect prompted us to calculate the Arrhenius activation energy for diffusion, \( E_D \), and permeation, \( E_p \), according to the relation (Eq. III.9). The values of \( E_D \) and \( E_p \) were estimated from the least square fitting of the linear plots of \( \log X \) versus \( 1/T \). Figures VII.8 and

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VII.9 display the Arrhenius plots for all the liquids. The values $E_D$ and $E_P$ are presented in Table VII.4.

**Table VII.4 Activation Energies for Diffusion and Permeation, and Heat of Sorption of Chloroalkanes and Chloroalkenes for Fluoroelastomeric Membrane.**

<table>
<thead>
<tr>
<th>Liquids</th>
<th>$E_P$ (kJ/mol)</th>
<th>$E_D$ (kJ/mol)</th>
<th>$\Delta H_S$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dichloromethane</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>46.37 ± 1.47</td>
<td>39.60 ± 1.44</td>
<td>6.77</td>
</tr>
<tr>
<td>Chloroform</td>
<td>34.22 ± 2.55</td>
<td>14.81 ± 2.12</td>
<td>19.41</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>16.20 ± 2.61</td>
<td>11.88 ± 6.54</td>
<td>4.32</td>
</tr>
<tr>
<td>Carbontetrachloride</td>
<td>42.55 ± 2.58</td>
<td>21.23 ± 1.16</td>
<td>21.32</td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>58.48 ± 1.28</td>
<td>51.23 ± 1.08</td>
<td>7.25</td>
</tr>
<tr>
<td>1,1,2,2-Tetrachloroethane</td>
<td>34.69 ± 3.33</td>
<td>24.71 ± 1.00</td>
<td>9.98</td>
</tr>
</tbody>
</table>

It is noticed that $E_D$ and $E_P$ values do not show any regular trend with the size of the penetrant. For chloroalkanes, the $E_D$ values range from 14.81 to 39.60 kJ/mol, for chloroalkenes, they range from 11.88 to 51.23 kJ/mol. Using the results of $E_D$ and $E_P$, we have calculated the heat of sorption as: $\Delta H_S = E_P - E_D$. The results so obtained are included in Table VII.4.

The $\Delta H_S$ gives the additional information about the molecular transport of liquid penetrants through the polymer matrix. The $\Delta H_S$ is a composite parameter.
involving contributions from both the Henry’s law and the Langmuir’s type of sorption. In the present study, the $\Delta H_S$ values are found to be positive, suggesting that sorption is mainly dominated by the Henry’s law, i.e., the formation of sites and the filling of these sites by the penetrant molecules. Hence the process of sorption is endothermic.

![Graph](image)

**Fig. VII.8** Arrhenius plots of log $D$ versus $1/T$ for fluoroelastomer membrane for (•) carbontetrachloride, (■) 1,2-dichloroethane and (▲) chloroform.
Fig. VII. 9 Arrhenius plots of log $D$ versus $1/T$ for fluoroelastomer membrane for (Δ) 1,1,2,2-tetrachloroethane, (□) tetrachloroethylene and (o) trichloroethylene.

VII.5 CONCLUSIONS

The transport of chloroalkanes and chloroalkenes through Fluorel (FC-2177D) membrane has been studied using the sorption gravimetric method. The results of these studies are important in the successful applications of these materials in separation science, barrier coatings in packaging, etc. The sorption coefficients determined in the present study decreased with increasing the size of the penetrants, except for dichloromethane. The low sorption coefficient observed for dichloromethane is attributed to the loss of solvent due to desorption/evaporation, since dichloromethane is a low boiling liquid as compared to others. The $D$ values increased systematically with increasing temperature, and show systematic dependence on the size of the penetrants, only in cases of 1,2-dichloroethane,
tetrachloroethylene and 1,1,2,2-tetrachloroethane. The other liquids such as chloroform, trichloroethylene and carbontetrachloride did not show dependence on the size of molecules. The trichloroethylene has the largest $D$ value of $5.92 \times 10^{-8}$ cm$^2$/sec among the liquids studied at 30°C. The permeability coefficients showed the same effect as those of diffusivity. Molecular transport is found to follow the anomalous type of behaviour in all the cases over the investigated temperature range. The liquid concentration profiles are dependent on the diffusivity values and temperature as well. The $E_D$ values range from 14.81 to 39.60 and 11.88 to 51.23 kJ/mol for chloroalkanes and chloroalkenes, respectively. The $\Delta H_S$ values are positive in all the cases, suggesting that the sorption is mainly dominated by endothermic contribution and following Henry's mode of sorption. The membrane is stable in all the liquids chosen as evidenced by no chemical degradation. Hence, the membrane (FC-2177D) studied here can be used in field applications containing these liquids.

VII.6 REFERENCES


